PROCESS FOR RECYLING COLORED THERMOPLASTIC MOLDED ARTICLES

This application is a Non-Provisional Utility application which claims priority under 35 U.S.C. § 119 on the basis of U.K. Patent Application No. 0224072.9 filed October 16, 2002, entitled "Process For Recycling Colored Thermoplastic Molded Articles" which is hereby incorporated by reference.

We, Fuquan Zeng, a citizen of China, residing at 17 Mill Croft, Cowling, Yorkshire, BD22 0AJ, United Kingdom, and Mark Frost, a citizen of the United Kingdom, residing at 9-15 Unity Grove, Knowsley Business Park, Knowsley, Merseyside, L34 9GT, United have invented a new and useful "Process For Recycling Colored Thermoplastic Molded Articles."

Background of the Invention

This invention relates to a process for recycling colored thermoplastic molded articles, polymer colorant additive compositions and their use and to recyclable materials. In particular it relates to a colorant additive composition and its use for addition to thermoplastic molding compositions and to recyclable molded articles containing said additive.

Field of the Invention

Polyethylene terephthalate is widely employed in the manufacture of packaging items. One large application for polyethylene terephthalate is in the manufacture of food packaging items and, in particular, beverage bottles. Such beverage bottles are extensively utilised for carbonated soft drinks and are increasingly more attractive, for safety considerations, in the packaging of alcoholic beverages such as beer. Bottles used for still or carbonated water or other soft drinks are typically colorless, green or blue. However, in the case of beer, it is conventional to provide an amber colored bottle in order to protect the contents from the deleterious effects of ultra-violet light.

Other uses for polyethylene terephthalate molding compositions include the manufacture of packages for agrochemicals, cosmetics, detergents and the like.

Polyethylene terephthalate bottles are usually manufactured using a two stage process. Granules of polyethylene terephthalate, along with any relevant additives, are injection molded in a first step to produce a preform. The resulting preform is then blow molded, possibly at a different factory, in a second step to the desired shape. Machines are also available which make bottle preforms and then blow them immediately into bottles.

Coloring of the preform is typically achieved by including a colorant additive with the polyethylene terephthalate granules. The colorant additive may be added as

a solid master batch in the form of granules or powder. Alternatively, the colorant additive may be suspended or dissolved in a liquid carrier in order to ensure a uniform dispersion of the colorant throughout the polyethylene terephthalate. The liquid carrier is generally an inert material, such as a hydrocarbon oil, an ester, an alcohol, or a mixture of two or more thereof. The liquid carrier is selected to be non-toxic, to have good compatibility with polyethylene terephthalate and to possess good solvent properties (if the colorant additive is to be dissolved in the liquid carrier). Ideally, the quantity of carrier included in the composition is kept to a minimum in order that the properties of the polyethylene terephthalate are not adversely affected.

Typical temperatures required for injection molding of polyethylene terephthalate molding compositions are between about 260 C and about 285 C or higher, e.g. up to about 310 C. When producing a colored preform it is desirable to select a colorant additive composition which will withstand these conditions. Somewhat lower temperatures in excess of about 100 C up to about 170 C or more are generally used in the blow molding step to produce a bottle from a polyester preform.

It is a recognised phenomenon within the industry that use of extended dwell times at elevated temperatures, particularly during the injection molding step used to make a polyethylene terephthalate bottle preform but also possibly during the subsequent blow molding step, may tend to result in an inferior

coloration of the preform or blow molded bottle. Therefore, much effort has been invested in finding colorant additives which have good stability and coloring properties at these temperatures.

It is further recognised that, with an increase in usage of polyethylene terephthalate and other thermoplastic materials for manufacture of packaging and other articles, a greater need arises to address the problem of disposal of the waste material. With land fill space becoming evermore scarce and with society being generally more environmentally aware than ever before, there is an increasing demand that the recycling option be taken. A limited amount of recycled polyethylene terephthalate material is already employed to produce strapping for packaging. Recycled polyethylene terephthalate is also used in the fibre industry to provide such products as wadding and sound insulation for cars and carpets. However, a more satisfactory option would be to recycle colored packaging of a sufficient quality such that it may be reused for food applications. Presently, colorless polyethylene terephthalate material may be recycled or reused either with or without the addition of coloring, and green colored material may be recycled to produce further green bottles. However, heretofore the recycling of certain colored polyethylene terephthalate bottles has proved to be problematic because it has proved difficult to recycle such bottles into materials of acceptable color. One such example is amber, which color precludes its use in new colorless or green bottles or in fibre applications.

Another thermoplastic material which is widely used in the packaging industry is so-called "crystal" polystyrene. This material also requires the use of high temperatures during processing. Typical molding temperatures for this material range from about 220 C to about 300 C. Other thermoplastic materials which are in wide spread use include polyolefins, such as polyethylene and polypropylene, and polyvinyl chloride.

It would be desirable to be able to recycle previously used colored thermoplastic materials, such as colored polyethylene terephthalate or colored "crystal" polystyrene, of any color in order to produce a material whose color would permit it to be recycled for further use, for example for food packaging or for use in fibre applications. In particular it would be desirable to be able to recycle used amber colored polyethylene terephthalate beer bottles in such a way as to produce, for example, a colorless or near colorless material or a green material which can then be utilised in the manufacture of further articles, such as blow molded articles.

It is possible to coat a colorless bottle with a coloring agent which may then be simply washed off for recycling of the bottle. However, this is an expensive option and is therefore unattractive when considering the high volume of recyclable material to be handled.

It is well known within the industry that polyethylene terephthalate does not exhibit good gas barrier properties. When producing bottles which will be used to package carbonated drinks or alcoholic beverages it is desirable to prevent carbon dioxide from escaping and being replaced by oxygen. It has accordingly been proposed to add a polyamide to the thermoplastic polyester molding composition in order to confer improved gas barrier properties on it. Alternatively a sandwich construction may be used in which nylon or an ethylene/vinyl alcohol resin is incorporated in a multi-layer preform which is then blow molded to form a bottle having improved gas barrier properties.

There is a need to provide a polymer colorant additive composition for incorporation into molding compositions (for example molding compositions which comprise polyethylene terephthalate and/or other polyesters) which is stable to the conditions required for injection molding but which will not render the colored molding composition unfit for recycling. There is a further need to provide a colored polyester molding composition which, after having been formed into bottles or other molded articles, is suitable for recycling to make further bottles or other articles of a commercially acceptable color.

There is a further need to provide colored blow molded articles, such as bottles, and colored preforms therefor, which exhibit good gas barrier properties and which provide protection for the contents against ultra-violet light, and which have a good recycling potential.

Object of the Invention

It is an object of the present invention to provide recycling potential to colored articles made from thermoplastic materials (such as polyethylene terephthalate or "crystal" polystyrene) where that has not been possible previously due to restrictions placed upon the utility of the recycled material as a result of its color.

Summary of the Invention

According to the invention there is provided a process for recycling a thermoplastic molded article comprising:

a) providing a thermoplastic molded article incorporating as colorant at least one thermolabile sublimable colorant;

b) subjecting the material of the molded article to elevated temperature conditions for a period of time sufficient to extract at least some of the thermolabile sublimable colorant and form an at least partially color modified composition; and

c) recovering the color modified composition for further recycling steps.

According to one aspect of the present invention there is provided a colorant additive composition for addition to a thermoplastic molding composition, said additive composition comprising at least one thermolabile sublimable colorant uniformly dispersed in an inert liquid carrier therefor, said inert liquid carrier being compatible with said thermoplastic molding composition.

The thermolabile sublimable colorant is substantially stable during the formation of a molded article from the thermoplastic molding composition. In order to mold such articles it is necessary to heat the composition to a temperature above its softening point. However, it is normally preferred to perform molding at a temperature below the melting point of the polymer material present in the thermoplastic molding composition. In the practice of the present invention, it will often be preferred to utilise polymer materials in the molding composition which can tolerate, or which require the use, high processing temperatures, for example temperatures of at least about 200°C. Some molding processes may require the use of more severe processing conditions than others. For example, in the formation of a blow molded polyethylene terephthalate bottle, injection temperatures in the range of from about 260°C to about 285°C or more, e.g. up to about 310°C, can be used in the course of forming a bottle preform whereas a lower temperature of, for example, from about 100°C up to about 170°C is typically used, in combination with a suitable high air pressure of , for example, about 40 bar, in order to blow a bottle of the desired shape from the bottle preform. The thermolabile sublimable colorant is preferably selected such that under the processing conditions and swell times used in manufacturing the molded article, no substantial sublimation and/or migration of the colorant occurs.

Polyethylene terephthalate used for injection molding purposes is typically post-condensed and has a molecular weight in the region of about 25,000 to 30,000.

However, it has also been proposed to use a fibre grade polyethylene terephthalate which is cheaper but is non-post-condensed, with a lower molecular weight in the region of about 20,000. It has further been suggested to use copolyesters of polyethylene terephthalate which contain repeat units from at least 85 mole % terephthalic acid and at least 85 mole % of ethylene glycol. Dicarboxylic acids which can be included, along with terephthalic acid, are exemplified by phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid and sebacic acid. Other diols which may be incorporated in the copolyesters, in addition to ethylene glycol, include diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentane-2,4-diol, 2-methyl pentane-1,4-diol, 2,2,4-trimethylpentane-1,3-diol, 2-ethylhexane-1,3-diol, 2,2-diethylpropane-1,3-diol, hexane-1,3-diol, 1,4-di(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane. In this specification the term "polyethylene terephthalate" includes not only polyethylene terephthalate but also such copolyesters.

Injection molding of polyethylene terephthalate and other polyester molding compositions is typically carried out using an injection molding machine and a maximum barrel temperature in the range of from about 260°C to about 285°C or

more, for example, up to about 310°C. The dwell time at this maximum temperature is typically in the range of from about 15 seconds to about 5 minutes or more, preferably from about 30 seconds to about 2 minutes.

When the molded article is recycled it may at some stage of the recycling procedure be exposed to conditions effective to sublime the thermolabile sublimable colorant and cause said colorant to migrate to the atmosphere. Mechanical recycling procedures may involve the following steps:

1. Collection (e.g. of bottles). This is usually organised through bottle collection points and some times by street collection.

2. Color sorting. This is often done manually although more in-line automated systems are becoming available. The commercial value of polyethylene terephthalate colored bottles is: clear > blue > green> amber/other transparent and translucent colors > opaque. Clear, blue and green can be blended to give an acceptable final resin color. Other colors find use either in strapping and staple fibre. There are also some applications in crates and pallets.

3. Grinding. Typically the bottles are ground into fragments of typical thickness 0.15 to 0.4 mm in size of approximately 1 to 2 cm.

4. Separation of polyethylene terephthalate from contaminants. This is usually done by flotation or other means such as air separation. This removes closures, labels, internal barrier layers, soil etc.

5. Washing. Typical composition of a wash is 1.8% sodium hydroxide. Bottles are typically washed at 80 to 85°C. This removes external barrier layers, plus more importantly, microbiological material and potentially toxic compounds.

6. Drying. Usually by hot air.

7. Extrusion and pelletizing. A vacuum pump is employed to remove volatiles. 8. Solid stating. This is usually conducted by convected heating at from about 220°C to about 240°C for 2 to 3 hours. This increases the IV to the required level. For bottle blowing this is typically 0.72 - 0.84 dL/g.

By appropriate choice of thermolabile sublimable colorant and recycling conditions, exposure of the molded article to these recycling steps, in particular steps 7 and 8, can extract some or all of the thermolabile sublimable colorant from the material of the molded article, thereby causing said material to undergo a desirable color change. For example, a green colored composition may by this procedure (involving the solid stating procedure in stage 8) be converted to a blue colored composition, or a red colored composition can be converted to a colorless or near colorless composition, or an amber colored composition may be converted to a substantially colorless composition or a green colored composition. However, this list of color changes is not exhaustive and many other color changes utilising the teachings of the invention can be achieved. Hence in a typical procedure the color of the material of the molded article comprising the thermolabile sublimable colorant can be changed by exposing it to solid stating conditions comprising a temperature of at least about 200°C for at

least about two hours. This procedure is extremely useful for enabling recycling of colored polyester molded articles, such as amber colored beer bottles, for re-use, since the undesirable amber color, from the point of view of the recycler, can be converted by use of the invention to an acceptable color for recycling, such as green or even colorless or near colorless.

The polymer colorant additive composition of the present invention includes a polymer-compatible organic liquid carrier. Such a carrier must be compatible with the polymer material of the thermoplastic molding composition and is preferably also compatible with the other components to be included in the thermoplastic molding composition of the invention. Typical carriers include hydrocarbons, hydrocarbon mixtures, alcohols, esters and mixtures of two or more thereof. Preferably the polymer-compatible organic liquid carrier is an oil based vehicle. Examples of such vehicles of the materials available as Clearslip TM 2 and ClearslipTM 3 from ColorMatrix Europe Ltd., of Unit 9-11, Unity Grove, Knowsley Business Park, Knowsley, Merseyside, L34 9GT.

The polymer colorant additive composition may also include one or more non-thermolabile and/or non-sublimable colorants, in addition to the at least one thermolabile sublimable colorant, if desired.

The polymer colorant additive composition may also comprise a plurality of thermolabile sublimable dyes. Differently colored thermolabile sublimable dyes

may be chosen in the additive composition in relative proportions to achieve a desirable color effect with or without combination with one or more non-thermolabile and/or non-sublimable colorants.

The thermolabile sublimable colorant may comprise a solvent or disperse dye. Such dyes may be dissolved or dispersed in the organic liquid carrier but are soluble in the polymer material of the thermoplastic molding composition and produce a uniform coloration of the final article. Suitable solvent dye groups include anthraquinone, indanthrone, monoazo, diazo, methine, quinophthalone, perinone, naphthalidimide and thioindigo dyes. The colorant additive composition may contain a single dye or a mixture of dyes depending upon the desired coloration of the article. For example, in order to produce an amber colored bottle there may be required a mixture of a red dye, a yellow dye and a blue dye. Examples of suitable dyes for use in the present invention also include solvent dyes such as the anthraquinones Violet 13 and Red 111 and Solvent Yellow 114.

The amount of colorant additive composition to be used in the thermoplastic molding composition can vary widely depending upon the final coloring effect and color strength desired in the finished article. The colorant additive composition is made by mixing the dry colorant or colorants in the form of a powder with a liquid organic carrier, typically in a range of from about 1 to about 85 wt %, more usually in the range of from about 30 to about 50 wt %. The resulting colorant

additive composition comprising the thermolabile sublimable dye or dyes uniformly dissolved or dispersed in the liquid carrier can then be added to the polymer in ranges from about 0.0001% by weight to about 7% by weight, for example, from 0.01% by weight up to about 5% by weight, based upon the weight of polymer component used.

It is not desirable to use higher concentrations of the colorant as this may interfere with the properties of the polymer material.

The polymer colorant additive composition may comprise a mixture of a red colorant, a blue colorant, and a yellow colorant in proportions such as to impart an amber color to a bottle preform extruded therefrom or to a bottle blow molded from said bottle preform.

Also provided in accordance with the invention is a thermoplastic molding composition comprising a thermoplastic material with at least one thermolabile sublimable uniformly dispersed therein.

The invention also provides a molded article from such a thermoplastic molding composition.

The invention further provides a process for recycling a molded article which includes subjecting the molded article to sublimation conditions at some stage of the recycling process.

In another aspect of the present invention there is provided a method for making a molded article from a colored thermoplastic molding composition which comprises:

(a) providing a thermoplastic molding composition;

(b) admixing with the thermoplastic molding composition at least one thermolabile sublimable colorant material to form a colored thermoplastic molding composition;

(c) heating the colored thermoplastic molding composition; and

(d) molding the hot colored thermoplastic molding composition so as to form a molded article.

In such a method said at least one thermolabile sublimable colorant is preferably admixed with the thermoplastic molding composition in the form of a polymer colorant additive composition comprising said at least one thermolabile sublimable colorant uniformly dispersed in an inert liquid carrier therefor. However, it is alternatively possible to add the colorant or colorants in any convenient manner, for example in particulate form such a powder or in admixture with a solid carrier.

Preferably the colored thermoplastic molding composition is substantially free from carbon black and from inorganic pigments.

Typically the colored thermoplastic molding composition is injection molded to form a bottle preform and the resulting bottle preform is then blow molded to form a bottle.

The invention further provides a method of making a blow molded bottle from a polyester molding composition which comprises:

(i) providing a polyester molding composition;

(ii) admixing with the polyester molding composition at least one thermolabile sublimable colorant material to form a colored polyester molding composition;

(iii) heating the colored polyester molding composition;

(iv) extruding the hot colored polyester molding composition so as to form a bottle preform; and

(v) blow molding the bottle preform at a blow molding temperature so as to form a colored bottle.

Also provided in accordance with another aspect of the present invention is a method of making a useful article which comprises:

(A) providing a thermoplastic molding composition;

(B) admixing with the thermoplastic molding composition at least one thermolabile sublimable colorant material to form a colored thermoplastic molding composition;

(C) forming a colored molded article by a procedure including heating the colored thermoplastic molding composition and molding said hot composition into a molded article;

(D) after use of the molded article, subjecting the material of the molded article to recycling steps which include subjecting the material of the molded article to elevated temperature conditions for a period of time sufficient to cause said material of the molded article to undergo a desirable change of color as a result of sublimation and migration to the atmosphere of at least some of the colorant material; and

(E) re-forming the thus treated material into a useful article.

The elevated temperature conditions to which the material of the molded article is subjected in the recycling stage (D) are selected to be sufficient to cause said desirable change of color in the molded article material. The variables in the conditions include temperature and time of exposure and may include pressure.

In one preferred process according the invention, the sublimated colorant is recovered and may then be re-used.

In the re-forming step (E) typically techniques that can be used include molding, extrusion, and other conventional processes for making articles of plastics materials, including fibres.

In such a method the colored thermoplastic (e.g. polyester) molding composition in step (B) can be injection molded to form a bottle preform and then the resulting bottle preform can be blow molded to form a bottle.

The invention further provides a method of making an article from a colored thermoplastic molding composition which comprises:

(I) providing a colored thermoplastic molding composition comprising recycled colored thermoplastic material, said recycled colored thermoplastic material containing at least one thermolabile sublimable colorant material;

(II) subjecting the colored thermoplastic molding composition to elevated temperature conditions for a period of time sufficient to extract at least some of the thermolabile sublimable colorant and form an at least partially color modified composition; and

(III) extruding the resulting at least partially color modified composition to form said article.

The article of step (III) may be a molded article, such as a bottle preform, or a fibre or any other useful article, such as a tube, a crate, or the like.

Polyethylene terephthalate is hygroscopic and after a period of approximately one year it is noticeable that preforms made of polyethylene terephthalate have taken up moisture from the air. Therefore, prior to the injection molding process, polyethylene terephthalate granules for use in the invention are preferably dried

for at least about 6 hours at from about 160 C to about 190 C, in a procedure which gives a slightly tactile product. The polyethylene terephthalate granules are transferred directly from the drier to the hopper of the injection molding machine. The polymer colorant additive composition of the current invention can then be added to and mixed with the polymer granules upon charging to the hopper. The injection molding process typically occurs at between about 260°C and about 285°C , more preferably at about 270°C, and the polymer material has a dwell time within the machine of less than 1 minute. Longer dwell times may result in inferior coloration of the preform. Once the preform has been blow molded into an appropriate article, said article may be recycled by a suitable procedure which includes use of temperatures of up to about 300°C or greater and dwell times up to or in excess of 5 minutes. When injection molded into a preform, the recycled material exhibits a different color from that of the original colorant additive composition used and hence that of the material which has been recycled. For example the color change may be from amber to green, black to blue or amber to colorless.

The thermoplastic molding composition of the invention may be utilised to produce a multi-layer bottle comprising a layer of nylon or ethylene/vinyl alcohol copolymer sandwiched between layers of said molding composition. This is particularly effective when colorant additive compositions are employed which produce dark colored bottles (such as amber or green) as not only does the

bottle exhibit good gas barrier properties but also good ultra-violet light barrier properties.

The invention is further illustrated in the following examples in which temperatures are in °C and parts and percentages are by weight.

Example 1

A mixture was prepared from 15 parts of Violet 13 dispersed in 51 parts of ClearslipTM 1 as inert carrier. ClearslipTM 1 is available from ColorMatrix Europe Limited of Units 9-11, Unity Grove, Knowsley Business Park, Knowsley, Merseyside, L34 9GT.

0.1 parts of the resulting dispersion were introduced with 99.9 parts of Eastman 9921 W polyethylene terephthalate granules, which had previously been dried by heating for 4 hours at 170°C, into the feed hopper of an Engle 80 tc extrusion molding machine and extruded at a barrel temperature of 275°C with a dwell time at this temperature of about 2 minutes to form a number of bottle preforms, each weighing 34.5 grams.

Each of the bottle preforms had a satisfactory color.

The bottle preforms were then heated for a period of from about 20 seconds to about 40 seconds using radiant heaters to a temperature in the range of from

about 95°C to about 110°C and blow molded using air at 40 bar to form bottles having a capacity of 1 litre.

A number of the resulting bottles were recycled by a procedure in which they were shredded and fed to the inlet hopper of a granulating machine and then washed in a caustic wash solution comprising 1.8 % sodium hydroxide at a temperature of between about 80°C and 85°C for a period of about one hour. The dried granules were then extruded at a barrel temperature of about 275°C with a dwell time at this temperature of about 2 minutes, and then pelletised. The resulting pellets were subjected to solid stating conditions for approximately 2 hours at 230°C under vacuum producing substantially colorless pellets which were successfully extruded and blow molded to form bottles of satisfactory appearance and properties.

Example 2

Example 1 was partially repeated using Solvent Red 111 in place of Violet 13 to produce molded bottle preforms containing 100ppm Solvent Red 111. The bottle preforms were reground and then loaded into a vacuum oven at 220°C for 16 hours. After this vacuum extraction the reground PET was molded into a plaque and color was measured, showing that 70% of the dye had been removed.